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RAMAN AND PHOTO-MODULATED REFLECTIVITY STUDIES OF ZnTe/InAs SEMICONDUCTOR HETEROSTRUCTURE UNDER HYDROSTATIC PRESSURE

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The photo–modulated reflectivity spectrum of a biaxially-strained pseudomorphic ZnTe epilayer, grown on an InAs epilayer by molecular beam epitaxy is studied as a function of applied hydrostatic pressure at 80K. With increasing hydrostatic compression, the biaxially compressive strain is progressively compensated by the pressure induced tensile strain. At approximately 55 kbars the epilayer becomes strain free, and is under a biaxial tension at higher pressures. The separation between the heavy hole and light hole signatures is superlinear in pressure, suggestive of a pressure dependent shear deformation potential constant for the valence and conduction bands. We also compare the pressure dependence of the Raman LO phonon of the ZnTe epilayer on InAs with that of a bulk ZnTe sample at 13K. The pressure dependent strain is found to be linear. Accurate values of the first order strain derivatives of the LO-phonons and mode Grüneisen constants are obtained.

It has been shown that ZnSe films grown pseudomorphically on GaAs exhibit pressure dependent strain effects through photomodulated reflectivity (PR)[1], photoluminescence (PL)[2] and Raman scattering[3] studies under pressure. It was also shown that the tetragonal deformation potential b is either a function of strain or volume deformation.[1,2] In this paper, we present a detailed photomodulated reflectivity (PR) and Raman study of a ZnTe epilayer grown on an InAs homoepitaxial epilayer.

The thin film samples consisted of a 63 nm epilayer of ZnTe grown on the (001) surface of a 1.5 µm thick InAs homoepitaxial epilayer on an InAs substrate by molecular beam epitaxy (MBE); bulk crystalline ZnTe was also studied. Experimental details are available elsewhere.[1]

The built-in strains in the epilayer due to the lattice mismatch are characterized by

$$\varepsilon = \varepsilon_{xx} = \varepsilon_{yy} = \frac{a_s - a_e}{a_e}, \quad \varepsilon_{zz} = -2\frac{c_{12}}{c_{11}}\varepsilon,$$
$$\varepsilon_{xy} = \varepsilon_{yz} = \varepsilon_{zx} = 0 \tag{1}$$

where a_s and a_e are the lattice constants of the substrate and the epilayer, respectively, and c_{ij} are the elastic constants. The direction of growth of the epilayer is taken as the z-axis and $\varepsilon = \varepsilon_{xx} = \varepsilon_{yy}$ is referred to as the biaxial strain.

Hydrostatic pressure decreases the lattice constants of a material. Since the compressibilities of different semiconductors vary, there can be pressure induced biaxial strains between semiconductors that share a common interface. The strain thus generated in a hetero-structure can be formulated quantitatively from expressions for the change of the respective lattice constants. Murnaghan's equation of state[4] can be written as

$$a(P) = a(1 \text{ bar})\left[\frac{B'}{B}P + 1\right]^{\frac{-1}{3B'}} \tag{2}$$

where a(P) is the lattice constant as a function of pressure, B is the bulk modulus ($=(c_{11}+2c_{12})/3$) and B' is the pressure derivative of the bulk modulus. The pressure-induced strain $\varepsilon(P)$ can be

expressed from Eq.(2) for the change in the respective lattice constants of the two materials as follows[1,2]:

$$\varepsilon(P) = \frac{a_s(P) - a_e(P)}{a_e(P)} \qquad (3a)$$

$$\varepsilon(P) = \varepsilon(0) + \left(\frac{a_s}{a_e}\right)\left[\frac{P}{(c_{11}+2c_{12})_e} - \frac{P}{(c_{11}+2c_{12})_s}\right] \qquad (3b)$$

where P is the applied hydrostatic pressure, and the c_{ij}'s are the elastic constants for the epilayer (e) and the substrate (s). In Eq. (3b), the initial lattice mismatch strain is $\varepsilon(0)$ and only a first order term in pressure is retained. If the bulk modulus of the epilayer is smaller than that of the substrate, as is the case in the system under consideration (table 1), then the pressure-induced stress is biaxially tensile.

We have measured the pressure dependence of the Raman active LO-phonon up to three orders for the ZnTe film on InAs and the bulk ZnTe, both samples loaded next to each other in the same diamond anvil cell. This has enabled us to directly measure the pressure dependence of the phonon shift $\Delta\omega$ of the film with respect to that of the bulk. Figure 1 shows the first and second order Raman spectra at different pressures for the ZnTe film on InAs (dotted lines) and the bulk ZnTe (solid lines). At 1 bar, (not shown) the first order LO-phonon in the film occurs at ~1cm^{-1} higher than that in the bulk. Under the applied pressure, the phonon peaks of the film and the bulk approach each other and coalesce at ~65 kbars. This is evident from Fig. 1 and also in Fig. 2, in which the average separation $\Delta\omega$ between the LO phonon in the film and the bulk ZnTe, is shown.

The shift $\Delta\omega$ of the LO-phonon of a strained epilayer film from its bulk counterpart is related to the strain components of the film grown along the [001] axis by[5]

$$\frac{\Delta\omega}{\omega} = \frac{\tilde{K}_{11}}{2}\varepsilon_{zz} + \frac{\tilde{K}_{12}}{2}(\varepsilon_{xx}+\varepsilon_{yy}) = \left(\tilde{K}_{12} - \tilde{K}_{11}\frac{c_{12}}{c_{11}}\right)\varepsilon \qquad (4)$$

Here the $\tilde{K}_{ij}$ denote first-order strain derivatives of the LO-phonon of the film material. These are related to the mode Grüneisen parameter γ_{LO} which is in turn related to the bulk modulus, B, and the pressure derivative of the LO-phonon according to

$$\tilde{K}_{11} + 2\tilde{K}_{12} = -6\,\gamma_{LO} \qquad (5a)$$

$$\gamma_{LO} = \frac{B}{\omega_{LO}}\frac{d\omega}{dP}. \qquad (5b)$$

From an analysis of the data we obtain $\gamma_{LO} = 0.99 \pm 0.04$, for the film and the bulk,

which is in agreement with an earlier measurement.[6] We also obtain values for K_{11} and K_{12} to be (-2.3±0.3) and (-1.7±0.3), respectively. Using the data from Fig. 2 and Eqs. (4-5), we have determined that the strain in the ZnTe film as a function of pressure is linear.

Figure 3 shows the photo-modulated reflectivity spectra of the ZnTe film on InAs at 80K. At 1 bar, two signatures at 2.383 eV and 2.419 eV correspond to the excitons associated with the heavy and light hole valence to conduction band transitions. The spectra are fitted to the functional form given in ref. 1 to yield energy, width, asymmetry, and relative intensities of the transitions. The PR signals could be observed only up to 62 kbar, a pressure at which InAs undergoes a phase transition into the rocksalt structure.

As the applied pressure is increased, the heavy and light hole transitions approach each other and cross at 55 kbars. Beyond 55 kbars, the character of the fundamental gap of the sample changes from heavy-hole to light-hole related.

The data were fit to the functional form $E(P) = E(0) + \alpha P + \beta P^2$. The linear and quadratic pressure coefficients are shown in table 2. From the average of the α's from we can compute the hydrostatic deformation potential a_{cv} for ZnTe[7] to be -5.0 ± 0.2 eV from the equation: $\alpha_{avg} = -a_{cv}/B$.

The splitting between the heavy and light hole transitions, $(E_g^{hh} - E_g^{lh})$, as a function of pressure is shown in Fig. 4 noting that[8]

$$E_g^{hh} - E_g^{lh} = 2\,\delta E_s + \frac{2\,\delta E_s^2}{\Delta} \qquad (6)$$

$$\delta E_s = -b\left(\frac{c_{11} + 2\,c_{12}}{c_{11}}\right)\varepsilon \qquad (7)$$

From the splitting of the heavy and light hole bands, $(E_g^{hh} - E_g^{lh})$, at 1bar and the lattice mismatch strain of -6.61×10^{-3} we find the shear deformation potential constant[7] $b = -1.27 \pm 0.05$ eV from Eqs.1, 6, and 7.

The pressure dependence in Fig. 4 is clearly strongly superlinear. The strain induced mixing of the light hole band and the spin-orbit split band, leads to a nonlinear term in Eq.(6). However, due to the large value of Δ (910 meV at 300K[9]), it is too small to account for the measured superlinearity. Hence $(E_g^{hh} - E_g^{lh})$ vs. pressure is given by $2\,\delta E_s$ which depends on b, c_{ij} and $\varepsilon(P)$.

The dotted curve in Fig. 4 is due to the strain calculated from Eq.3a and the value of b obtained from the 1bar data. The agreement is good up to
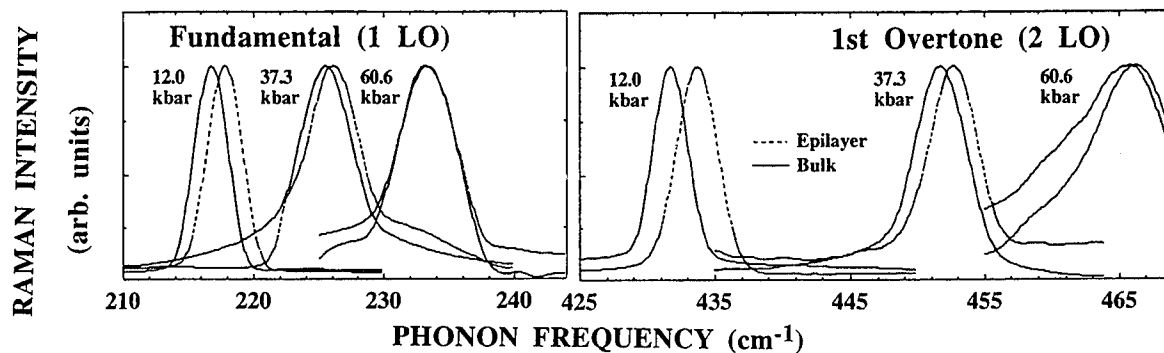
Figure 1: The first and scond order Raman spectra of the LO phonon of the ZnTe film on InAs(dotted line) and of bulk ZnTe(solid lines) at different pressures and 13K.
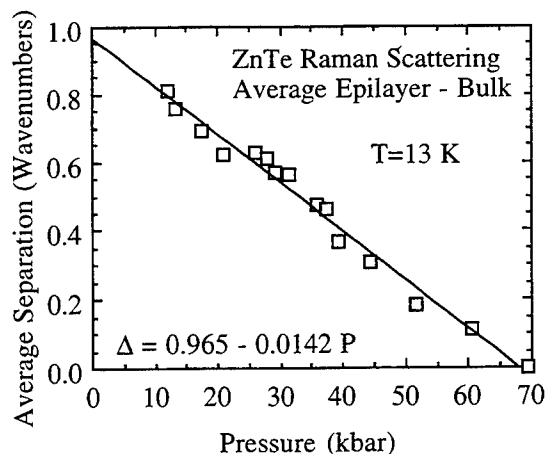

Figure 2: The average separation of the LO phonon of the film and the bulk ZnTe vs. pressure.
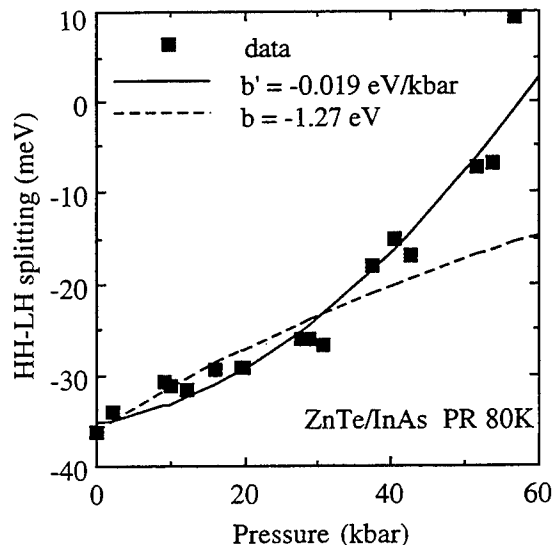

Figure 4: The separation between the heavy and light hole transitions plotted versus pressure.
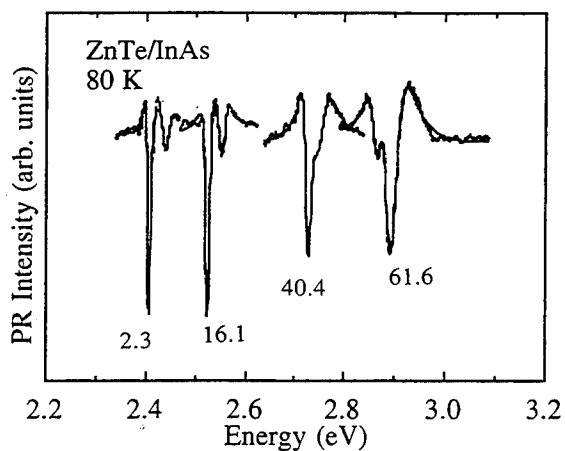

Figure 3: The photomodulated reflectivity spectra of ZnTe film on InAs vs. pressure in kbars.

Table 1: Physical Constants[9]

	B(kbar)	B'	C_{12}/C_{11}
ZnTe	521	4.7	0.57
InAs	613	4.79	0.54

Table 2: Pressure Coefficients

	α(meV/kbar)	β(meV/kbar^2)
Heavy Hole	8.96±0.20	-0.013±0.002
Light Hole	9.45±0.20	-0.034±0.003

30 kbar; at higher pressures it indicates a slight sublinear rather than the observed superlinear pressure dependence. By allowing a small pressure dependent term b′ (= db/dP) for the tetragonal deformation potential b, the fit can be improved as shown by the solid curve. The values obtained from the fit are b = −1.21 eV and b′ = −0.019 eV/kbar.

It should be noted here that similar effects were observed in the case of a pseudomorphic ZnSe film on GaAs. The Raman data[3] showed a linear pressure dependent strain whereas the PR and PL data[1,2] gave evidence for a pressure dependent tetragonal deformation potential. Both the ZnTe/InAs and ZnSe/GaAs systems seem to indicate that the electronic bands in the film deviate from the linear deformation potential theory, whereas the lattice vibrations are in the linear regime.

Both the Raman and PR data clearly show that the effect of applied pressure is to cancel the initial mismatch strain. The pressure P_m at which the cancellation occurs was found to be ~55 kbar from the PR data at which the splitting of the heavy and light hole bands goes to zero. In the Raman data the difference in frequency of the Raman phonon of the film and that in a separate bulk sample was compared. A somewhat higher (~65 kbar) value of the observed P_m is probably due to the uncertainty in the initial (1 bar) separation $\Delta\omega$. A decrease of ~0.2 cm^{-1} in this value will bring the P_m in agreement with the PR data.

In conclusion, pressure tuning of the biaxial strain in ZnTe epilayers pseudomorphically grown on InAs is observed by Raman scattering and photo-modulated reflectivity studies. Values for the deformation potential constants, mode Grüneisen parameters and first order strain derivatives of the LO phonon are determined. The Raman data shows a linear dependence of the strain vs. pressure. The PR data indicate that the tetragonal deformation potential depends on pressure (or volume) in a manner similar to that observed in ZnSe epilayers on GaAs.

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